



Hydrogen production by steam gasification of polypropylene with various nickel catalysts

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ABSTRACT

Several nickel-based catalysts (Ni/Al₂O₃, Ni/MgO, Ni/CeO₂, Ni/ZSM-5, Ni-Al, Ni-Mg-Al and Ni/CeO₂/Al₂O₃) have been prepared and investigated for their suitability for the production of hydrogen from the two-stage pyrolysis–gasification of polypropylene. Experiments were conducted at a pyrolysis temperature of 500 °C and gasification temperature was kept constant at 800 °C with a catalyst/polypropylene ratio of 0.5. Fresh and reacted catalysts were characterized using a variety of methods, including, thermogravimetric analysis, scanning electron microscopy with energy dispersive X-ray spectrometry and transmission electron microscopy. The results showed that Ni/Al₂O₃ was deactivated by two types of carbons (monoatomic carbons and filamentous carbons) with a total coke deposition of 11.2 wt.% after reaction, although it showed to be an effective catalyst for the production of hydrogen with a production of 26.7 wt.% of the theoretical yield of hydrogen from that available in the polypropylene. The Ni/MgO catalyst showed low catalytic activity for H₂ production, which might be due to the formation of monoatomic carbons on the surface of the catalyst, blocking the access of gaseous products to the catalyst. Ni-Al (1:2) and Ni-Mg-Al (1:1:2) catalysts prepared by co-precipitation showed good catalytic abilities in terms of both H₂ production and prevention of coke formation. The ZSM-5 zeolite with higher surface area was also shown to be a good support for the nickel-based catalyst, since, the Ni/ZSM-5 catalyst showed a high rate of hydrogen production (44.3 wt.% of theoretical) from the pyrolysis–gasification of polypropylene.

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1. Introduction

Hydrogen is seen as a key future fuel for the low carbon energy systems of the future because water is the only product of combustion and it has the potential to dramatically reduce our dependence on fossil fuels. For example, hydrogen for power generation and as a transport fuel has been identified. Power generation from hydrogen fuel cells and hydrogen fuelled turbines has the potential to provide a clean source of future energy production. Hydrogen fuelled vehicles where the hydrogen is combusted directly or via fuel cell technology would generate zero carbon emissions. However, the sustainable benefits of hydrogen fuel cell technology lie with the source of the production process for the hydrogen. At present hydrogen is largely produced either from fossil fuel sources such as natural gas, naphtha and coal or via water electrolysis, photolysis or thermolysis. However, processes involving fossil fuels involve high temperatures, requiring high

inputs of energy and generate significant carbon dioxide during the process. There is therefore growing interest in the production process for hydrogen based around alternative feedstocks.

One such feedstock source for the production of hydrogen is waste plastic where, for example, using pyrolysis–gasification large molecules of the plastic can be broken down to produce H₂ [1]. In 2004, about 13 million tonnes of waste plastic was generated throughout Western Europe, however, the recycling rate for the plastic was less than 10%, representing a waste of a valuable resource [2]. In addition, the recycling technologies for waste plastic tend to be low grade, for example, high density polyethylene are recycled as dustbin sacks and pipes and garden furniture, polyvinylchloride are recycled for sewer pipes, shoes, electrical fittings and flooring. Processing applications for mixed post-consumer plastic waste include plastic fencing, industrial plastic pallets, traffic cones, plastic lumber [3]. Therefore, from an economic and environmental perspective, producing hydrogen from plastics is a promising technology; however, the technical challenge is to increase production efficiency of H₂ from the gasification of plastic waste.

A key factor in maximising the production of hydrogen from waste plastics using pyrolysis–gasification is the use of catalysts.

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There are few data on the use of catalysts for hydrogen production from waste plastics, however, research into their use in gasification of biomass is extensive [3–5]. Due to some similarities in the composition of products from the thermal degradation of biomass, the use of the same type of catalysts for the gasification of waste plastics is of interest [6–8].

Nickel-based catalysts are commonly used by researchers in biomass gasification as they are effective for tar reduction and hydrogen production [9–12]. Although noble metals such as Ru and Rh are reported to be more effective than nickel-based catalysts, they are not commonly used in industry because of their high cost [13]. Nickel-based catalysts could be effective for hydrogen production from plastics [14,15]. A typical and suitable support for Ni catalysts is Al_2O_3 , because of its chemical and physical stability and high mechanical properties [11]. However, the deactivation of Ni/ Al_2O_3 catalyst caused by nickel sintering and carbon deposition is a significant problem for the utilization of nickel catalysts. Therefore, many researchers have tried to improve the properties of Ni/ Al_2O_3 catalysts by introducing metals or using different preparation methods. Cerium and magnesium have been particularly investigated due to their abilities to prevent coke formation on the catalyst [9,10]. In addition, magnesium has been introduced in many commercial nickel catalysts used for steam gasification of biomass [16,17]. Zeolite was found to be effective as a support for nickel catalysts for biomass gasification [18]. Different preparation processes of nickel catalysts such as co-impregnation instead of incipient wetness have been reported to be effective to improve catalyst performance during the gasification of hydrogen carbon feedstocks [19,20].

In this paper, several supports (Al_2O_3 , MgO, CeO_2 and ZSM-5) for nickel catalysts and different preparation processes for nickel-based catalysts (incipient wetness, co-impregnation and co-precipitation) were investigated for their effectiveness in the production of hydrogen from the pyrolysis–gasification of polypropylene.

2. Materials and methods

2.1. Materials

Polypropylene was obtained as 2 mm virgin polymer pellets provided by BP Chemicals, UK.

Seven types of nickel-based catalysts were prepared in the laboratory. The metal oxides were obtained from Sigma–Aldrich, UK. ZSM-5 zeolite (CBV 8014) was provided by Zeolyst International PA, US. Ni/ Al_2O_3 ($\gamma\text{-Al}_2\text{O}_3$), Ni/ CeO_2 , Ni/MgO and Ni/ZSM-5 were prepared by an incipient wetness method using an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and various supports, followed by drying at 105 °C overnight. After drying, the catalysts were calcined at 750 °C for 3 h under an air atmosphere, except the Ni/ZSM-5 catalyst (10 wt.% Ni) which was calcined at 500 °C.

Ni/ $\text{CeO}_2/\text{Al}_2\text{O}_3$ was prepared by a co-impregnation method. $\gamma\text{-Al}_2\text{O}_3$ was impregnated with the aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ mixture. The catalyst was dried at 105 °C overnight, and then calcined at 500 °C for 3 h in an air atmosphere. The loading of Ni was 10 wt.%, and that of CeO_2 was 30 wt.%.

Ni–Al (molar ratio 1:2) and Ni–Mg–Al (molar ratio 1:1:2) were prepared using the rising pH technique according to the method reported by Garcia et al. [21]. The precipitant, 1 M NH_4OH , was added to 200 ml of an aqueous solution containing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with or without the addition of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The precipitation was carried out at 40 °C with moderate stirring until the final pH (7.9 for Ni–Al catalyst, 8.3 for Ni–Mg–Al catalyst) was obtained. The precipitates were filtered with water (40 °C),

followed by drying at 105 °C overnight, and then they were calcined at 750 °C for 3 h.

All the catalysts used in this paper were crushed and sieved to granules with a size of less than 0.212 mm. In addition, all the catalysts used were not reduced. The gases produced during the process, such as H_2 and CO, possess the ability to reduce the catalyst in situ [18,19].

2.2. Characterization of catalysts

The BET (Brunauer, Emmett and Teller) surface area of each catalyst was obtained via nitrogen adsorption experiments using a Quantachrome Corporation (FL, US) Autosorb 1-C Instrument.

The thermal decompositions of polypropylene in terms of weight loss behaviour with or without catalyst were carried out using a Stanton-Redcroft thermogravimetric analyser (TGA). The sample was heated in an atmosphere of nitrogen at 20 °C min^{-1} to a final temperature of 700 °C, with a dwell time of 10 min. The temperature-programmed oxidation (TPO) of coked catalysts (around 100 mg) was carried by TGA in an atmosphere of air at 15 °C min^{-1} to a final temperature of 800 °C, with a dwell time of 10 min.

Two different Scanning electron microscopes (SEM) were used to examine the catalysts. A Phillips XL30 Environmental SEM coupled to an energy dispersive X-ray spectroscopy (EDXS) system was used to investigate the surface morphology and the elements distributions of fresh catalysts. A higher resolution SEM (LEO 1530) was used to determine the characteristics of the carbon on the coked catalysts. Transmission electron microscopy (TEM) (Philips CM200) was used to determine the coked Ni/ $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst. For the TEM analysis, the sample was ground, dispersed with ethanol, and then deposited on a Cu grid covered with a perforated carbon membrane.

2.3. Experimental system

The pyrolysis–gasification of polypropylene was carried out with a two-stage fixed bed reactor. A schematic diagram of the experimental system is shown in Fig. 1. The polypropylene was pyrolysed in the first stainless tube reactor, and then gasified in the second stainless tube reactor. Both of these tubes were 16 cm in length with an internal diameter of 2.2 cm, and each was separately heated externally by an electrical furnace and continually purged with nitrogen. At the start of each experiment, approximately 1.0 g of polypropylene was placed in the pyrolysis reactor and 0.5 g catalyst, supported on quartz wool, was placed in the second gasification reactor. Water, provided by a syringe pump, was introduced into the reactor (just after the pyrolysis of polypropylene and before the catalyst) where it was converted into steam as a gasification agent. The flow rate of water used was 4.74 ml h^{-1} .

The first reactor was heated to 500 °C where pyrolysis of the polypropylene took place, the evolved pyrolysis gases were passed directly to the second reactor heated to 800 °C, where gasification in the presence of the catalyst and steam took place. For practical purposes, the gasification reactor was heated to 800 °C and when the temperature was stabilised, the pyrolysis of the polypropylene was commenced with a heating rate of 40 °C min^{-1} to the final pyrolysis temperature of 500 °C. Examination of the thermal degradation profile of polypropylene showed that the decomposition commenced at about 420 °C and was complete by 500 °C with a reaction time of 30 min. Therefore, water was introduced by a syringe pump when the temperature of the first reactor reached 400 °C. The gaseous products derived from the degradation of polypropylene in the first reactor were gasified in the second

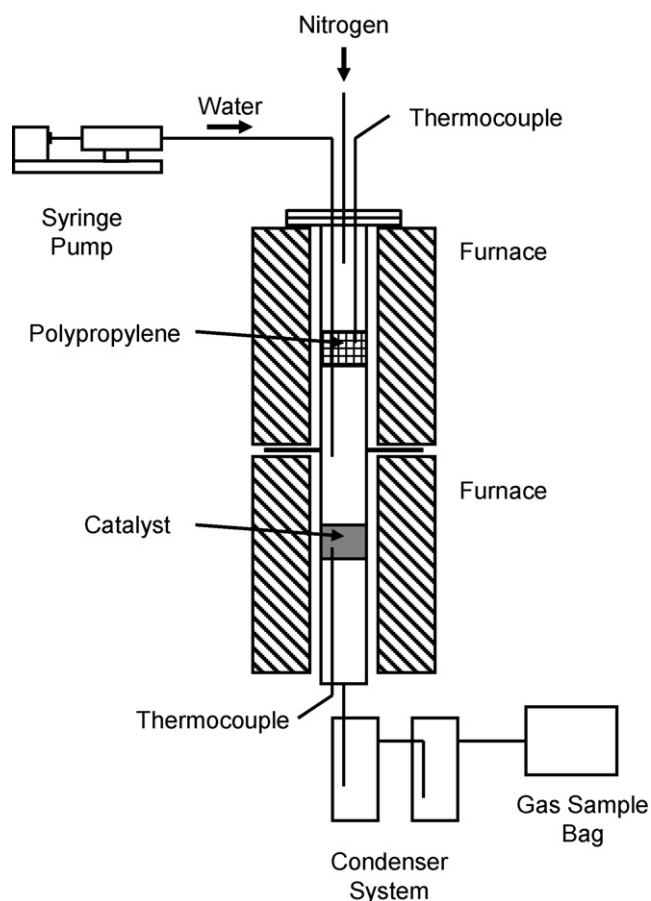


Fig. 1. Schematic diagram of the two-stage experimental system.

Table 1
BET surface area of research catalysts.

Catalyst	Loading or molar ratio	BET surface area ($\text{m}^2 \text{g}^{-1}$)
Ni/Al ₂ O ₃	10 wt.% Ni	90
Ni/MgO	10 wt.% Ni	32
Ni/CeO ₂	10 wt.% Ni	57
Ni/ZSM-5	10 wt.% Ni	261
Ni-Al	Molar ratio (1:2)	155
Ni-Mg-Al	Molar ratio (1:1:2)	118
Ni/CeO ₂ /Al ₂ O ₃	10 wt.% Ni, 30 wt.% CeO ₂	287

3. Results and discussion

3.1. Characterisation of the fresh researched catalysts

Table 1 shows the surface areas for the catalysts produced for the investigation of hydrogen production from gasification of waste plastics. The Ni/ZSM-5 catalyst showed a high BET surface area, which was $261 \text{ m}^2 \text{g}^{-1}$. The addition of magnesium into the Ni-Al catalyst structure was found to reduce the BET surface area from 155 to $118 \text{ m}^2 \text{g}^{-1}$. The co-impregnation of Ni/CeO₂/Al₂O₃ also produced a catalyst with a comparatively high BET surface area of $287 \text{ m}^2 \text{g}^{-1}$. The nickel-based catalysts with metal oxides as supports produced by wetness showed a lower BET surface area than those catalysts produced via co-impregnation and co-precipitation. For example, the BET surface area for Ni/Al₂O₃ catalyst was $90 \text{ m}^2 \text{g}^{-1}$, while for Ni/MgO it was only $32 \text{ m}^2 \text{g}^{-1}$.

A 10 wt.% Ni/MgO catalyst was produced by a wetness process at the calcination temperature of 800°C for hydrogen production from the gasification of lignin in the report of Furusawa et al. [3]. The BET surface area of the produced catalyst was found to be $34.0 \text{ m}^2 \text{g}^{-1}$. The result is close to the one produced in this paper, which shows a surface area of $31.7 \text{ m}^2 \text{g}^{-1}$ at the calcination temperature of 750°C . Catalysts with 4 wt.% Ni loaded on Al₂O₃ and 30 wt.% CeO₂/Al₂O₃ supports where the γ -Al₂O₃ was converted to α -Al₂O₃ was reported by Nishikawa et al. [22]. They reported that the BET surface areas of Ni/Al₂O₃ and Ni/CeO₂/Al₂O₃ were 9 and $13 \text{ m}^2 \text{g}^{-1}$, respectively. Catalysts with 12 wt.% Ni/Al₂O₃, 12 wt.% Ni/MgO and 12 wt.% Ni/CeO₂ were prepared by Miyazawa et al. for the steam reforming of tar [23]. The BET surface areas of Ni/Al₂O₃, Ni/MgO and Ni/CeO₂ were reported to be 8, 12, $12 \text{ m}^2 \text{g}^{-1}$, respectively. The surface areas of Ni-Al (1:2) ($150 \text{ m}^2 \text{g}^{-1}$) and Ni-Mg-Al (1:1:4) ($108 \text{ m}^2 \text{g}^{-1}$) catalysts were also reported by Garcia et al. [21].

A preliminary investigation of the potential influence of each catalyst on the thermal degradation of the polypropylene was undertaken using thermogravimetric analysis (TGA). The polypropylene was intimately ground and mixed with each catalyst with a catalyst/polypropylene ratio of 0.5 and analysed to determine weight loss in relation to temperature in a nitrogen atmosphere using TGA. The results are presented in Fig. 2. The calculation of weight ratio was carried out as follows:

$$w = \frac{W_i - W_r}{W_i - W_r}$$

where w is the weight ratio; W_i is the weight at each experimental temperature; W_i is the initial weight; and W_r is the residue weight at the end of experiment.

In the absence of any catalyst the polypropylene showed a maximum weight loss between 475 and 500°C . Fig. 2 shows that the Ni/ZSM-5 catalyst dramatically promoted the thermal degradation of polypropylene, illustrated by the on-set of weight loss at a temperature of 200°C . The catalytic influence on degradation temperature of the Ni/ZSM-5 catalyst to the pyrolysis

reactor with steam, then exited the reactor system, and passed through an air-cooled condenser and a dry-ice cooled condenser where liquid products were collected. Finally, all uncondensed gases were collected with a 10 L TedlarTM gas bag. The gases were collected for more than 20 min after each experiment to insure all of the gases were collected. The amount of consumed water in each experiment was calculated from the weight difference of injected water and the condensed water. In most of the experiments, condensed oil in the condensers could be neglected. And the water consumption was also adjusted with the oxygen content in the CO and CO₂ gases.

The gaseous products collected in the TedlarTM sample bag were analysed by two separate gas chromatographs. Hydrocarbons from C₁ to C₄ were determined using a Varian 3380 gas chromatograph with a flame ionisation detector (GC/FID). Nitrogen was used as a carrier gas with a $2 \text{ m} \times 2 \text{ mm}$ column packed with 80–100 mesh Hysesp. The oven temperature was set at 60°C for 3 min, then programmed to 100°C at the heating rate of 5°C min^{-1} , and held for 3 min, finally ramped to 120°C at $20^\circ\text{C min}^{-1}$ and held for 17 min. Permanent gases (H₂, CO, O₂, N₂ and CO₂) were analysed by a second Varian 3380 GC with two packed columns and with two thermal conductivity detectors (GC/TCD). Hydrogen, oxygen, carbon monoxide, methane and nitrogen were analysed on a 2 m length by 2 mm diameter column, packed with 60–80 mesh molecular sieve. Argon was used as the carrier gas. Carbon dioxide was analysed on a 2 m length by 2 mm diameter column with Haysep 80–100 mesh packing material. The gas chromatograph oven was held isothermally at 40°C for the analysis. The detector oven was operated at 120°C with filament temperature at 160°C .

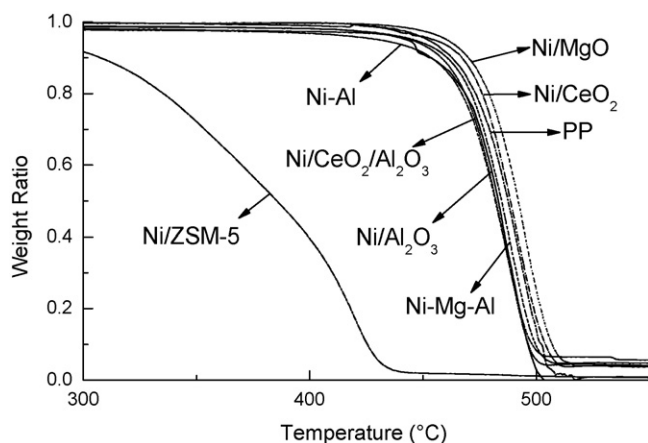


Fig. 2. TGA results for mixtures of polypropylene and each produced catalyst.

of polypropylene might be due to its well-defined structure and high surface area that reduced the reaction heat of pyrolysis. The other catalysts showed little influence on the degradation of polypropylene under the particular conditions of the experiment in the thermogravimetric analyser. Ni-Al, Ni/CeO₂/Al₂O₃, Ni/Al₂O₃ and Ni-Mg-Al catalysts showed a reduction of the degradation temperature of polypropylene, while Ni/CeO₂ and Ni/MgO catalysts showed an increase in the degradation temperature for the pyrolysis of polypropylene.

Figs. 3 and 4 show the scanning electron micrographs (SEM) and energy dispersive X-ray spectrograms (EDXS), respectively, for some selected catalysts. As was shown in Fig. 3, Al₂O₃ seems to be encased by CeO₂ and NiO for the Ni/CeO₂/Al₂O₃ catalyst. The SEM

of Ni/MgO catalyst shows typical granular characteristics. From Fig. 3, the SEM of Ni-Al and Ni-Mg-Al catalysts prepared by coprecipitation seem to be different from the ones produced by incipient wetness. The EDXS analysis also showed that the metals were dispersed well throughout the catalysts. The molar ratio of Ni and Al elements was about 1:2 for the Ni-Al catalyst and for the Ni-Mg-Al catalyst, the molar ratio of Ni, Mg and Al from EDXS analysis was around 1:1:2. These molar ratios of the catalysts were consistent with the original preparation.

3.2. Steam catalytic pyrolysis–gasification of polypropylene

3.2.1. Materials balance

The products of pyrolysis of polypropylene produced in the first reactor, prior to transfer to the second reactor, were examined to obtain the product distribution and gas composition. The results showed that without the second gasification stage, only 5.8 wt.% gaseous products were obtained, and 81.5 wt.% oil/wax was produced, the other products were char and residue. Among the gaseous products, 22.0 vol% of H₂ was obtained, the other gases were hydrocarbons. It could be expected that more gases will be generated and reformed with the gasification stage.

Before the investigation of catalysts, silica sand was substituted for the catalyst in the gasification reactor as a baseline experiment to determine any reactions of the pyrolysis gases with a particle surface. The product yields are shown in Table 2. The results of the pyrolysis–gasification of the polypropylene experiment, with no catalyst (sand) and no steam, demonstrated that no liquid oil was obtained because of the high gasification temperature (800 °C). The products were gas and a solid fraction representing 39.3 and 52.9 wt.%, respectively, indicating that a large amount of char was produced by carbonization. The solid fraction included residue

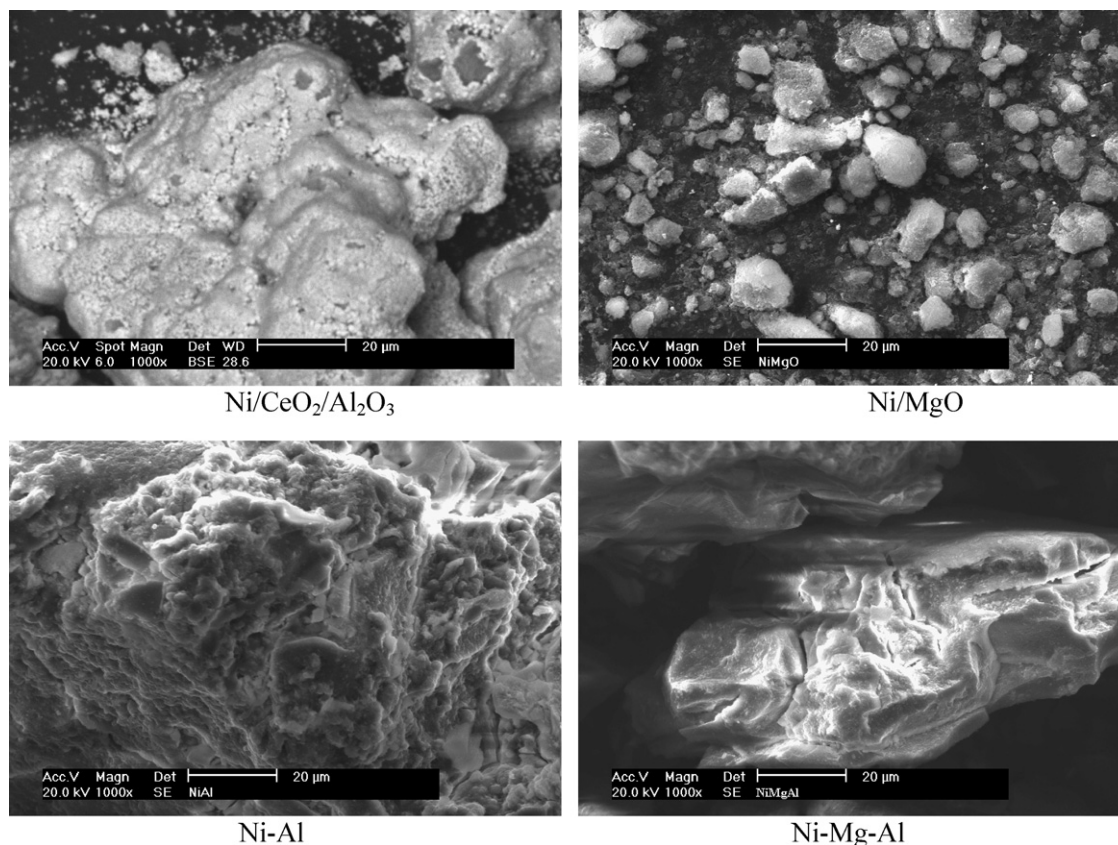


Fig. 3. SEM results of several produced catalysts.

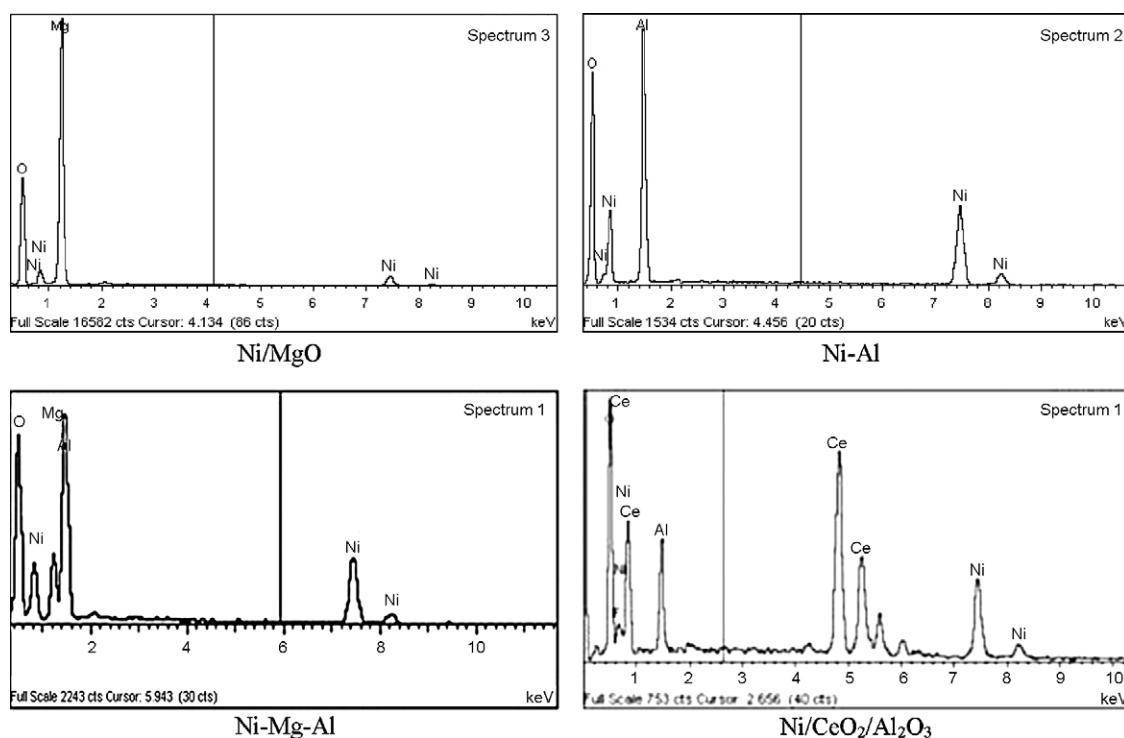


Fig. 4. EDXS results of some produced catalysts.

formed in the pyrolysis reactor and char and coke (on the reactor wall and catalyst) formed in the gasification reactor. The residue weight was obtained by the weight difference of the sample both before and after experiment. The char and coke amounts were calculated by the weight difference of the gasification reactor before and after experiment.

The introduction of steam to the second reactor in the presence of sand resulted in an increase in gas yield from 39.3 to 79.1 wt.%, and a reduction in solid char yield to 8.5 wt.% (Table 2). The water consumed was 0.05 g. Steam is known to be very effective for gas and hydrogen production through the gasification and water gas shift (WGS) reactions [24,25]. In the case of steam gasification of polypropylene with sand, a little yellow liquid (oil) was condensed and collected.

The influence of the various prepared catalysts on the gasification of polypropylene was investigated and the results are shown in Table 2. The results show that the gas yield was markedly increased in the presence of a catalyst, except the Ni/CeO₂ and Ni/MgO catalysts which showed only a little influence on gas yield. The Ni/ZSM-5 catalyst generated a high gas yield of 93.7 wt.% and low solid yield of 3.6 wt.%. ZSM-5 zeolite, with a specified pore size, high surface area and adjustable acid site, can be a promising support for Ni-based catalysts. Both Ni-Al and Ni-

Mg-Al catalysts showed a significant catalytic effluence on the pyrolysis–gasification of polypropylene. The introduction of magnesium into the Ni-Al catalyst system increased the gas yield from 96.0 to 99.1 wt.%, and reduced the solid yield from 2.8 to 0.6 wt.%. The reacted water for Ni-Mg-Al (1.29 g) was also higher than that for the Ni-Al (1.21 g) catalyst. The gas yield was also increased and the solid yield was decreased by introducing CeO₂ into the Ni/Al₂O₃ catalyst system. However, the water which reacted with Ni/CeO₂/Al₂O₃ catalyst was 1.05 g which was much higher than that for the Ni/Al₂O₃ catalyst (0.62 g).

The mass balances from the experiment without catalyst and Ni/MgO catalyst are slightly less than 90% and lower than that in other experiments. This might be due to the lower catalytic activity of Ni/MgO and sand which generated large amounts of hydrocarbon gases (Table 3). The amounts of C5 (especially n-pentane) or other hydrocarbons might not be collected and detected in the gas chromatographic system used in this work and resulted in an incomplete total gas weight.

3.2.2. Gas composition and hydrogen production

During the steam pyrolysis–gasification of polypropylene with or without catalyst, C₁–C₄ gases as well as hydrogen were produced. Their volumetric concentrations (on a nitrogen free

Table 2
Results of pyrolysis–gasification of polypropylene with or without different catalysts.

Catalyst bed	Gasification catalyst								
	Sand	Sand	Ni/CeO ₂ /Al ₂ O ₃	Ni/ZSM-5	Ni/Al ₂ O ₃	Ni/CeO ₂	Ni/MgO	Ni-Al	Ni-Mg-Al
Water flow rate (g h ⁻¹)	0.0	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7
Reacted water (g)	0.00	0.05	1.05	1.03	0.62	0.35	0.07	1.21	1.29
Yields (wt.%)									
Gas/(polypropylene + water)	39.3	79.1	90.8	93.7	89.7	64.9	77.9	96.0	99.1
Solid ^a /(polypropylene + water)	52.9	8.5	7.8	3.6	9.0	29.3	6.5	2.8	0.6
Mass balance	92.7	87.6	98.6	97.3	98.7	94.1	89.0	98.7	99.7

^a Solid fraction of products includes char, coke, soot and residue after reaction.

Table 3

Gas composition in the product gases (nitrogen free, vol%).

	Gas					
	H ₂	CO	CO ₂	CH ₄	C ₂ –C ₄	LHV (MJ m ^{−3})
Catalyst						
Sand (without water)	67.3	0.0	0.0	22.1	10.6	16.1
Sand	25.8	6.7	0.2	22	45.3	17.5
Ni/CeO ₂ /Al ₂ O ₃	63.8	22.9	8.1	3.6	1.6	11.5
Ni/ZSM-5	63.6	20.3	11.8	2.8	1.5	10.9
Ni/Al ₂ O ₃	56.3	20.0	9.3	6.1	8.3	13.1
Ni/CeO ₂	75.5	6.2	7.5	5.5	5.3	11.9
Ni/MgO	32.6	7.9	0.8	20.6	38.1	16.8
Ni–Al	64.0	25.7	6.4	3.3	0.6	11.5
Ni–Mg–Al	61.8	28.7	6.5	2.2	0.8	11.4

basis) in the product gases are shown in Table 3. The potential H₂ production from the experiment with or without catalyst is shown in Fig. 5. The maximum theoretical amount of H₂ produced from polypropylene steam gasification is estimated to be 42.9 g per 100 g polypropylene [1]. In this paper, the potential H₂ production was obtained which corresponded to the maximum H₂ production (42.9 g/100 g polypropylene). From Table 3, in the presence of sand (no catalyst) and no steam, there was no CO and CO₂ produced in the gas products. After introduction of water into the reactor system without a catalyst (sand), CO and CO₂ were generated with concentrations of 6.7 and 0.2 vol%, respectively. However, the introduction of steam resulted in the H₂ content of the gases being reduced to 25.8 vol% from 67.3 vol% compared to the un-catalysed pyrolysis–gasification of polypropylene without the presence of steam. The results suggest that the reduced concentration of hydrogen was due to a higher conversion of the polypropylene to C₂–C₄ in the presence of steam.

Table 3 and Fig. 5 show that the introduction of a catalyst resulted in an increase in hydrogen production. However, the Ni/MgO catalyst generated a large amount of methane corresponding to a low content of hydrogen and carbon dioxide. Sato et al. [26] investigated different Ni loadings on a MgO support for the gasification of lignin in supercritical water. The main gas products were reported to be methane, carbon dioxide, and hydrogen. They suggested that Ni metal particles and the MgO support played different roles in the gasification process. MgO catalysed reactions formed unstable lignin fragments and Ni particles promoted reactions between the intermediates and water.

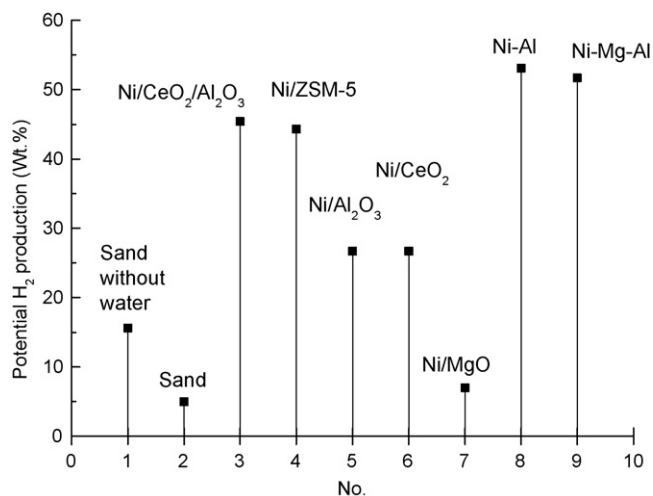
**Fig. 5.** Potential H₂ production from pyrolysis–gasification of polypropylene.

Table 3 and Fig. 5 show that the Ni/Al₂O₃ catalyst produced an increase in hydrogen yield compared to the results without the catalyst, since the potential hydrogen yield was about 26.7 wt%. However, the formation of coke on the catalyst was high and would result in deactivation of the Ni/Al₂O₃.

It has been reported that Ni–Al catalysts produced by co-precipitation have a higher catalytic activity than a Ni/Al₂O₃ catalyst, because of their larger metallic area and higher thermal stability [27]. The Ni–Al catalyst showed good catalytic ability for the production of hydrogen, with H₂ at 64.0 vol%, C₁–C₄ gases at 3.9 vol%, CO at 25.7 vol% and CO₂ concentration at 6.4 vol%. The potential hydrogen yield reached 53.1 wt% and therefore, it can be concluded that most of the hydrogen elements in the polypropylene were converted into hydrogen gas by the steam catalytic pyrolysis–gasification of polypropylene. Garcia et al. [27], investigated a Ni–Al catalyst in relation to biomass gasification, the catalyst had a molar ratio of 1:2 (Ni:Al) and was prepared by co-precipitation and calcined at 750 °C for 3 h. No reduction of the catalyst was carried out prior to the biomass gasification experiments. They reported that the addition of catalyst into the pyrolysis of biomass significantly increased the yields of hydrogen, carbon monoxide and carbon dioxide with a decrease in methane gas yield. Arauzo et al. [28] also researched a Ni–Al catalyst for the gasification of wood. They found a relatively high stability of Ni–Al catalyst for tar reforming at a temperature of 650 °C.

Table 3 also shows that the carbon monoxide concentration in the presence of the Ni–Al catalyst was very high. According to the water gas shift reaction, the highest hydrogen production would be obtained when the entire carbon monoxide is converted into carbon dioxide. It could be suggested that further addition of CO₂ absorbents could be made to increase the water gas shift reaction that favours the production of CO₂ and H₂.

In this paper, magnesium was introduced into the Ni–Al catalyst structure to improve the Ni–Al catalytic activity. From Table 3 and Fig. 5, the hydrogen production from the Ni–Mg–Al catalyst was slightly decreased after the addition of magnesium. For example, the H₂ concentration in the gas reduced from 64.0 to 61.8 vol% with the introduction of Mg into Ni–Al catalyst. However, the Ni–Mg–Al showed a better ability for prohibition of coke formation. Lower hydrogen production was also reported by Arauzo et al. [28], where they reported that the surface area and pore size of the catalyst was reduced by the substitution of magnesium for nickel. Arauzo et al. [28] also suggested that the addition of magnesium reduced the surface of the Ni–Al catalyst, where catalytic activity occurs. The other reason for the reduced catalytic activity of the Ni–Mg–Al catalyst they proposed was due to the Ni–Mg–Al catalyst requiring a high reducing temperature, of the order of 850–900 °C [29].

The influence on the catalytic behaviour of the addition of cerium in the catalytic gasification of polypropylene was investigated

by cerium addition to the Ni/Al₂O₃ catalyst to produce Ni/CeO₂/Al₂O₃. Table 3 shows that the concentrations of hydrogen and carbon monoxide were increased and C₁–C₄ gases decreased in concentration compared to gasification with the Ni/Al₂O₃ catalyst. Fig. 5 also shows that the theoretical potential hydrogen production was also increased from 26.7 to 45.4 wt.% with the addition of cerium to the Ni/Al₂O₃ catalyst system.

Table 3 and Fig. 5 show that the Ni/ZSM-5 catalyst produced hydrogen in significant concentrations from the catalytic gasification of polypropylene, where the concentration of hydrogen was 63.6 vol% and the potential hydrogen production was 44.3 wt.%. In addition, the concentration of carbon monoxide was 20.3 vol%, carbon monoxide 11.8 vol%, methane 2.8 vol% and C₂–C₄ gases were 1.5 vol%, respectively.

The lower heating value (LHV) of gaseous products derived from pyrolysis–gasification of polypropylene with various nickel catalysts were also shown in Table 3. The LHV results show that the lower heating value is between 10 and 16 MJ m^{−3} for the gases. With the higher catalytic activity, the LHV of gaseous products seem to be reduced.

3.3. Characterisation of coked catalysts

Coke deposition on the catalyst is one of the most common and serious problems in the pyrolysis–gasification of various polymers. In this section, the characteristics of coke formation on the various catalysts used in the catalytic steam pyrolysis–gasification of polypropylene were investigated.

Figs. 6 and 7 show the TGA and DTG results from the temperature-programmed oxidation (TPO) of the various coked catalysts. The weight ratio in Fig. 6 equals the weight at each temperature point divided by the initial sample (coked catalyst) weight. It seems that there is a moisture vaporization peak for each temperature-programmed oxidation (TPO) experiment at a temperature of around 100 °C. Fig. 8 shows the scanning electron micrographs (SEM) of the catalysts after reaction except the coked Ni/CeO₂/Al₂O₃ catalyst, which was analysed by TEM.

Around 11.2 wt.% coke was deposited on the Ni/Al₂O₃ catalyst as determined by the TGA–TPO experiment (Fig. 6). The coke amount was calculated from the weight loss of sample divided by the original sample weight. From the DTG–TPO experiments (Fig. 7), two oxidation peaks were observed. It seems that two types of carbon were formed on the Ni/Al₂O₃ catalyst after pyrolysis–gasification of polypropylene. The lower oxidation peak

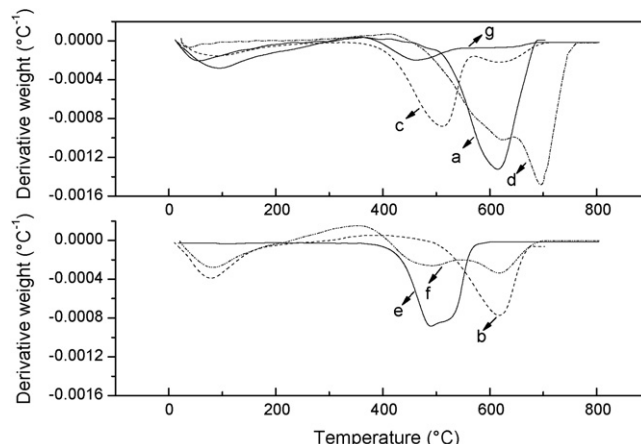


Fig. 7. DTG analysis of coked catalysts, (a) Ni/CeO₂/Al₂O₃; (b) Ni/ZSM-5; (c) Ni/Al₂O₃; (d) Ni/CeO₂; (e) Ni/MgO; (f) Ni-Al; (g) Ni-Mg-Al.

occurred at a temperature of 510 °C and might be assigned to monoatomic carbon [30]. The higher oxidation peak could be assigned to filamentous carbon [31]. The filamentous carbons were also observed by the SEM analysis for the reacted Ni/Al₂O₃ catalyst (Fig. 8). The diameters of the carbon nanofibers were around 20 nm for the reacted and coked Ni/Al₂O₃ catalyst. Davidian et al. [5] investigated the production of hydrogen from crude pyrolysis oil using a Ni/Al₂O₃ catalyst and reported the diameters of carbon fiber filaments formed on the catalysts to be between 10 and 30 nm. Takenaka et al. [32] investigated the structural change of Ni species on Ni catalysts during methane decomposition. The filamentous carbon type was also found by the authors and they reported that the diameters of the carbon nanofibers on the Ni/Al₂O₃ catalyst were smaller than 20 nm. They pointed out that the diameters of these carbon nanofibers increased with repeated use of the reacted catalyst. Therefore, although the Ni/Al₂O₃ catalyst proved to be effective for the production of hydrogen from the pyrolysis–catalytic gasification of polypropylene, the catalyst was prone to high carbon coking and deactivation. The deactivation of Ni/Al₂O₃ via coke formation has also been reported by other researchers [11,12,23].

Figs. 6 and 7 suggest that the Ni-Al catalyst seemed more effective for preventing coke formation than the Ni/Al₂O₃ catalyst. The amount of coke on the catalyst was reduced from 11.2 to 4.8 wt.% for the Ni/Al₂O₃ catalyst compared to the Ni-Al catalyst. A few filamentous carbons could be found in the SEM analysis of the Ni-Al catalyst. However, the diameters of the filamentous carbons on the Ni-Al catalyst were smaller than the ones on the Ni/Al₂O₃ catalyst. A Ni-Al catalyst was used for steam gasification of pine sawdust by Garcia et al. [27]. They also reported that the Ni-Al catalyst showed good performance to prevent the coke formation, since deactivation of the Ni-Al catalyst was not observed while the catalyst weight/biomass flow rate was higher than 0.65.

Magnesium oxide was also investigated as the support for the Ni catalyst. One oxidation peak is observed for the Ni/MgO catalyst in the DTG–TPO result (Fig. 7) at the temperature around 500 °C. This oxidation peak can be assigned to the monoatomic carbon deposited on the Ni/MgO catalyst. The higher oxidation peak might correspond to the filamentous carbon which is not found for Ni/MgO catalyst. This observation is proved by the SEM result of Ni/MgO (Fig. 8), where no filamentous carbon could be found. It is suggested that the monoatomic carbon gets deposited on the surface of Ni/MgO catalyst, and blocks the access of gases reactants to the catalyst. Therefore, resulting in a lower catalytic activity of Ni/MgO in the pyrolysis–gasification of polypropylene, in addition,

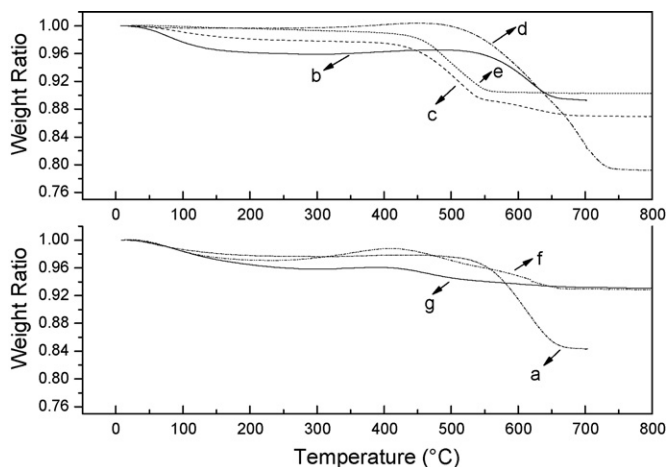


Fig. 6. TGA analysis of coked catalysts, (a) Ni/CeO₂/Al₂O₃; (b) Ni/ZSM-5; (c) Ni/Al₂O₃; (d) Ni/CeO₂; (e) Ni/MgO; (f) Ni-Al; (g) Ni-Mg-Al.

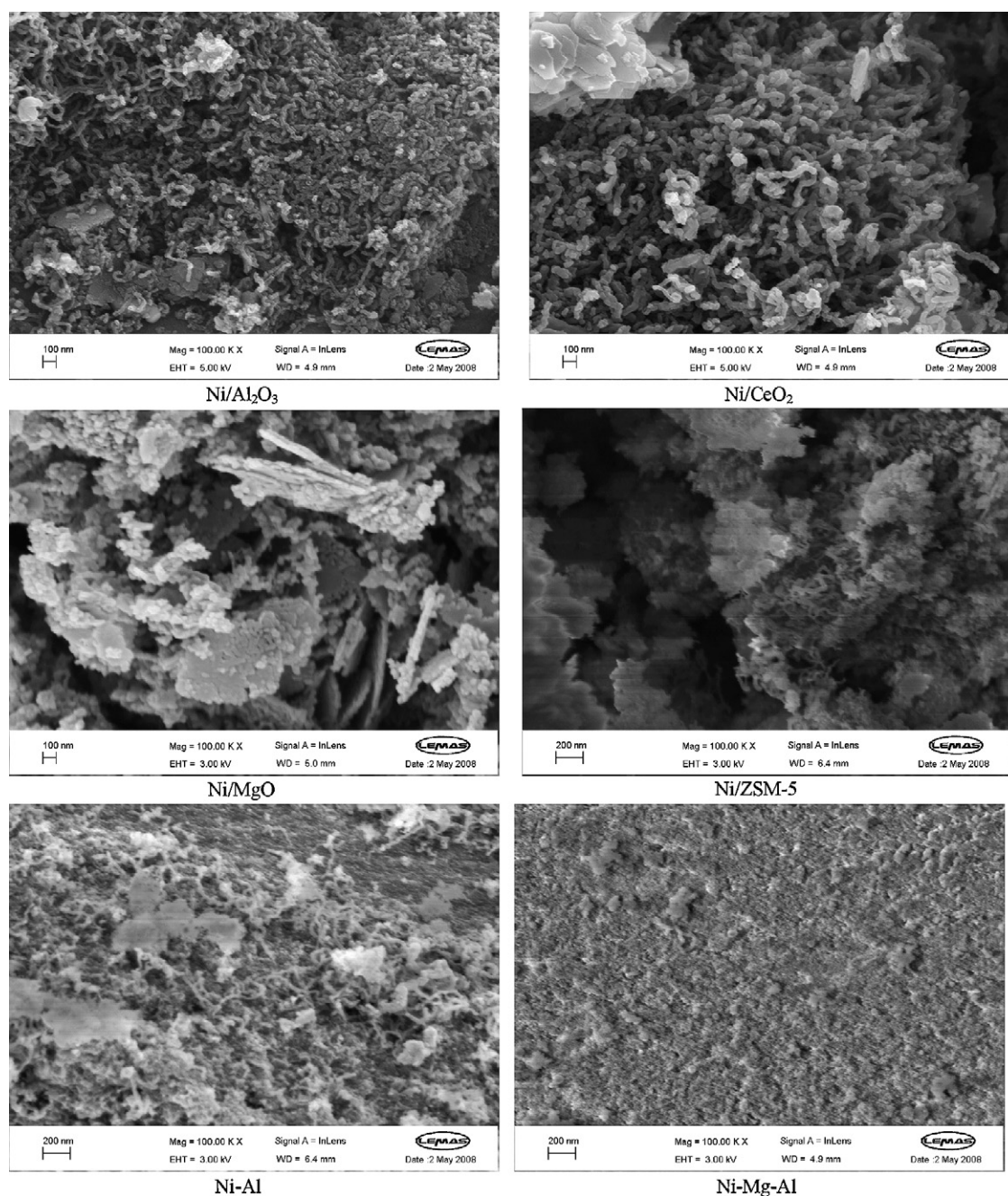


Fig. 8. SEM analysis of reacted catalysts.

large amounts of hydrocarbons were generated in the gas corresponding to a lower H₂ content (Table 3 and Fig. 5).

It is suggested that magnesium metal has the ability to enhance steam gasification of carbon or carbon precursors formed on the catalyst during the experiment, while the solid solution of NiO/MgO was reported to stabilise nickel and prevent catalyst sintering [33,34]. To investigate the effectiveness of magnesium addition in the production of hydrogen from the pyrolysis-catalytic gasification of polypropylene, magnesium was also introduced into Ni-Al catalyst structure to improve the stability of Ni-Al catalyst. Fig. 6 indicates that a small amount of coke is formed on the Ni-Al and Ni-Mg-Al catalysts during the experiments. It could be concluded that these two catalysts are effective to prevent coke formation during the pyrolysis-gasification of polypropylene. The coke formed on the Ni-Mg-Al catalyst was

reduced to 2.8 wt.% from 4.8 wt.% for the Ni-Al catalyst, yet the hydrogen production was still high. As shown in Fig. 7, the higher temperature oxidation peak (around 610 °C) disappears upon introduction of Mg into the Ni-Al catalyst; the higher temperature oxidation peak representing oxidation of filamentous carbons which was confirmed by SEM analysis of the Ni-Mg-Al catalyst surface which showed negligible filamentous carbon (Fig. 8). It is suggested that the introduction of Mg into the Ni-Al catalyst enhances the steam gasification of carbons, which might mostly be the filamentous type carbons. Therefore, higher concentrations of CO and CO₂ with Ni-Mg-Al were generated compared to the Ni-Al catalyst from the catalytic steam pyrolysis-gasification of polypropylene (Table 3).

The presence of cerium oxide in catalysts has been reported to be effective in the prevention of coke formation on the catalyst due

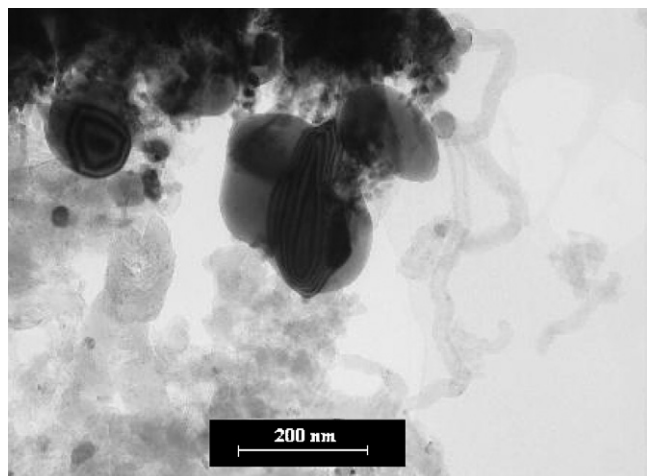


Fig. 9. TEM analysis of reacted Ni/CeO₂/Al₂O₃ catalyst.

to its high redox property [22,35]. However, Fig. 6 shows that large amounts of coke (around 20.5 wt.%) were deposited on the Ni/CeO₂ catalyst. The DTG–TPO result (Fig. 7) shows that the oxidation peak for the Ni/CeO₂ catalyst is around 700 °C, which indicates that a large amount of filamentous carbons were formed on the Ni/CeO₂ catalyst. The filamentous carbons were extensively observed by the SEM analysis with diameters of about 50 nm (Fig. 8). However, Inaba et al. [36] reported that there was no carbon deposited on a Ni/CeO₂ catalyst during the gasification of cellulose for hydrogen production.

In this paper, cerium oxide was also introduced into the Ni/Al₂O₃ catalyst as Ni/CeO₂/Al₂O₃. The results from TGA–TPO experiment (Fig. 6) and transmission electron microscope analysis (Fig. 9) indicated that the prevention of coke formation on the surface of the catalyst was not greatly improved with the addition of cerium. Filamentous carbons were found on the Ni/CeO₂/Al₂O₃ catalyst after pyrolysis–catalytic gasification reaction as shown in Fig. 9, which showed that the diameter of filamentous carbon was about 25 nm. The reduced effect of cerium addition for the Ni/CeO₂/Al₂O₃ catalyst might be due to the high loading of CeO₂ (30 wt.%), which resulted in the sintering of CeO₂ [22,37].

From Figs. 6 and 7, the Ni/ZSM-5 catalyst showed some deactivation after reaction. However, only a few filamentous carbons could be observed by the analysis using scanning electron microscopy. The low amount of filamentous carbons on the Ni/ZSM-5 catalyst was also indicated by the DTG–TPO experiment (Fig. 7), where the higher temperature oxidation peak shows low intensity. The lower temperature oxidation peak (lower than 550 °C) was not found in Fig. 7. This might demonstrate that little monoatomic carbons were formed on the Ni/ZSM-5 catalyst. The good performance of Ni/ZSM-5 catalyst in terms of the hydrogen and gas production (Table 3 and Fig. 5) suggests that the filamentous carbon has little influence on the catalytic activities in the pyrolysis–gasification of polypropylene.

4. Conclusions

Several laboratory prepared catalysts were investigated for the production of hydrogen from the pyrolysis–catalytic gasification of polypropylene in a two-stage reactor system. The results suggested that:

- (1) The Ni/Al₂O₃ catalyst prepared by incipient wetness was shown to be an effective catalyst for the production of hydrogen with

a 26.7 wt.% of theoretical stoichiometric potential hydrogen being obtained. However, it suffered from serious coke deposition and resulted in the deactivation.

- (2) The Ni/CeO₂/Al₂O₃ catalyst prepared by co-impregnation unexpectedly did not present the highest catalytic ability, especially for the prevention of coke formation, probably due to a too high content of CeO₂ (30 wt.%) in the catalyst [22].
- (3) The Ni–Al and Ni–Mg–Al catalysts prepared by co-precipitation showed a high catalytic ability for the production of hydrogen from polypropylene. The hydrogen productions of theoretical stoichiometric potential were 53.1 and 51.7 wt.% for the Ni–Al and Ni–Mg–Al catalysts, respectively. Both of these catalysts also exhibited low coke formation. With the introduction of Mg into the Ni–Al catalyst, the higher temperature oxidation peak assigned to filamentous carbon disappeared which was also confirmed by SEM analysis.
- (4) The Ni/ZSM-5 catalyst was found to be effective for the production of hydrogen from pyrolysis–catalytic gasification of polypropylene with 44.3 wt.% of potential hydrogen being obtained. And most of the carbons deposited on the Ni/ZSM-5 catalyst are the filamentous type, which show little influence on the catalytic activity.

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References

- [1] S. Czernik, R.J. French, *Energy Fuel* 20 (2006) 754.
- [2] APEME, Good practices guide on waste plastics recycling a guide by and for local and regional authorities, Association of Plastics Manufacturers in Europe, Brussels, Belgium, 2004.
- [3] T. Furusawa, T. Sato, H. Sugito, Y. Miura, Y. Ishiyama, M. Sato, N. Itoh, N. Suzuki, *Int. J. Hydrogen Energy* 32 (2007) 699.
- [4] S. Rapagna, H. Provendier, C. Petit, A. Kiennemann, P.U. Foscolo, *Biomass Bioenergy* 22 (2002) 377.
- [5] T. Davidian, N. Guilhaume, E. Iojoiu, H. Provendier, C. Mirodatos, *Appl. Catal. B: Environ.* 73 (2007) 116.
- [6] R. Xiao, B.S. Jin, H.C. Zhou, Z.P. Zhong, M.Y. Zhang, *Energy Convers. Manage.* 48 (2007) 778.
- [7] F.J. Mastral, E. Esperanza, C. Berruero, M. Juste, *J. Anal. Appl. Pyrolysis* 70 (2003) 1.
- [8] P. Vriesman, E. Heginuz, K. Sjostrom, *Fuel* 79 (2000) 1371.
- [9] D. Sutton, B. Kelleher, J.R.H. Ross, *Fuel Process. Technol.* 73 (2001) 155.
- [10] Z.A. El-Rub, E.A. Bramer, G. Brem, *Ind. Eng. Chem. Res.* 43 (2004) 6911.
- [11] P.A. Simell, J.O. Hepola, A.O. Krause, *Fuel* 76 (1997) 1117.
- [12] J. Srinakruang, K. Sato, T. Vitidsant, K. Fujimoto, *Catal. Commun.* 6 (2005) 437.
- [13] D.L. Trimm, *Catal. Today* 37 (1997) 233.
- [14] C. Courson, E. Makaga, C. Petit, A. Kiennemann, *Catal. Today* 63 (2000) 427.
- [15] S.C. Tsang, J.B. Claridge, M.L.H. Green, *Catal. Today* 23 (1995) 3.
- [16] M.P. Aznar, M.A. Caballero, J. Gil, J.A. Martin, J. Corella, *Ind. Eng. Chem. Res.* 37 (1998) 2668.
- [17] S. Czernik, R. French, C. Feik, E. Chornet, *Ind. Eng. Chem. Res.* 41 (2002) 4209.
- [18] M. Inaba, K. Murata, M. Saito, Presented at the Fifteenth World Hydrogen Energy Conference, Yokohama, Japan, June 27–July 1, 2004.
- [19] O. Clause, M. Gazzano, F. Trifiro, A. Vaccari, L. Zatorski, *Appl. Catal.* 73 (1991) 217.
- [20] O. Clause, B. Rebours, E. Merlen, F. Trifiro, A. Vaccari, *J. Catal.* 133 (1992) 231.
- [21] L. Garcia, A. Benedicto, E. Romeo, M.L. Salvador, J. Arauzo, R. Bilbao, *Energy Fuel* 16 (2002) 1222.
- [22] J. Nishikawa, T. Miyazawa, K. Nakamura, M. Asadullah, K. Kunimori, K. Tomishige, *Catal. Commun.* 9 (2008) 195.
- [23] T. Miyazawa, T. Kimura, J. Nishikawa, S. Kado, K. Kunimori, K. Tomishige, *Catal. Today* 115 (2006) 254.
- [24] S. Turn, C. Kinoshita, Z. Zhang, D. Ishimura, J. Zhou, *Int. J. Hydrogen Energy* 23 (1998) 641.
- [25] R. Martinez, E. Romero, L. Garcia, R. Bilbao, *Fuel Process. Technol.* 85 (2003) 201.
- [26] T. Sato, T. Furusawa, Y. Ishiyama, H. Sugito, Y. Miura, M. Sato, N. Suzuki, N. Itoh, *Ind. Eng. Chem. Res.* 45 (2006) 615.
- [27] L. Garcia, M.L. Salvador, J. Arauzo, R. Bilbao, *Energy Fuel* 13 (1999) 851.
- [28] J. Arauzo, D. Radlein, J. Piskorz, D.S. Scott, *Ind. Eng. Chem. Res.* 36 (1997) 67.
- [29] J.R. Rostrup-Nielsen, in: J.R. Andersen, M. Bourdard (Eds.), *Catalysts Science and Technology*, Springer, Berlin, 1984, p. 1.
- [30] S. Wang, G.Q. Lu, *Appl. Catal. B: Environ.* 19 (1998) 267.

- [31] S. Wang, G.Q. Lu, *Ind. Eng. Chem. Res.* 38 (1999) 2615.
- [32] S. Takenaka, E. Kato, Y. Tomikubo, K. Otsuka, *J. Catal.* 219 (2003) 176.
- [33] P.B. Tottrup, B. Nielsen, *Hydrocarb. Process.* (March) (1982) 89–91.
- [34] J.R.H. Ross, *Catalysts*, vol. 7, The Royal Society of Chemistry, London, 1985, pp. 1–45.
- [35] K. Tomishige, T. Kimura, J. Nishikawa, Tomohisa Miyazawa, Kimio Kunimori, *Catal. Commun.* 8 (2007) 1074.
- [36] M. Inaba, K. Murata, M. Saito, I. Takahara, *Energy Fuel* 20 (2006) 432.
- [37] M. Asadullah, T. Miyazawa, S. Ito, K. Kunimori, K. Tomishige, *Appl. Catal. A: Gen.* 246 (2003) 103.